National Energy Technology Laboratory

SOFC Interconnect Work at NETL

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RE Surface Treatment Results

- **Oxidation resistance of Crofer improved by 3x (800C/3% water/4,000h)**
  - Appears to minimize internal silica layer formation
- **Improved ASR (800C/500h)**
  - Button cell tests underway
- **Oxidation resistance of type 430 vastly improved**
  - Eliminated spall (800C/3% water/4,000h)
- **Effectively makes 12 Cr alloys perform as 22 Cr**

Improving Oxidation Resistance with Rare Earths

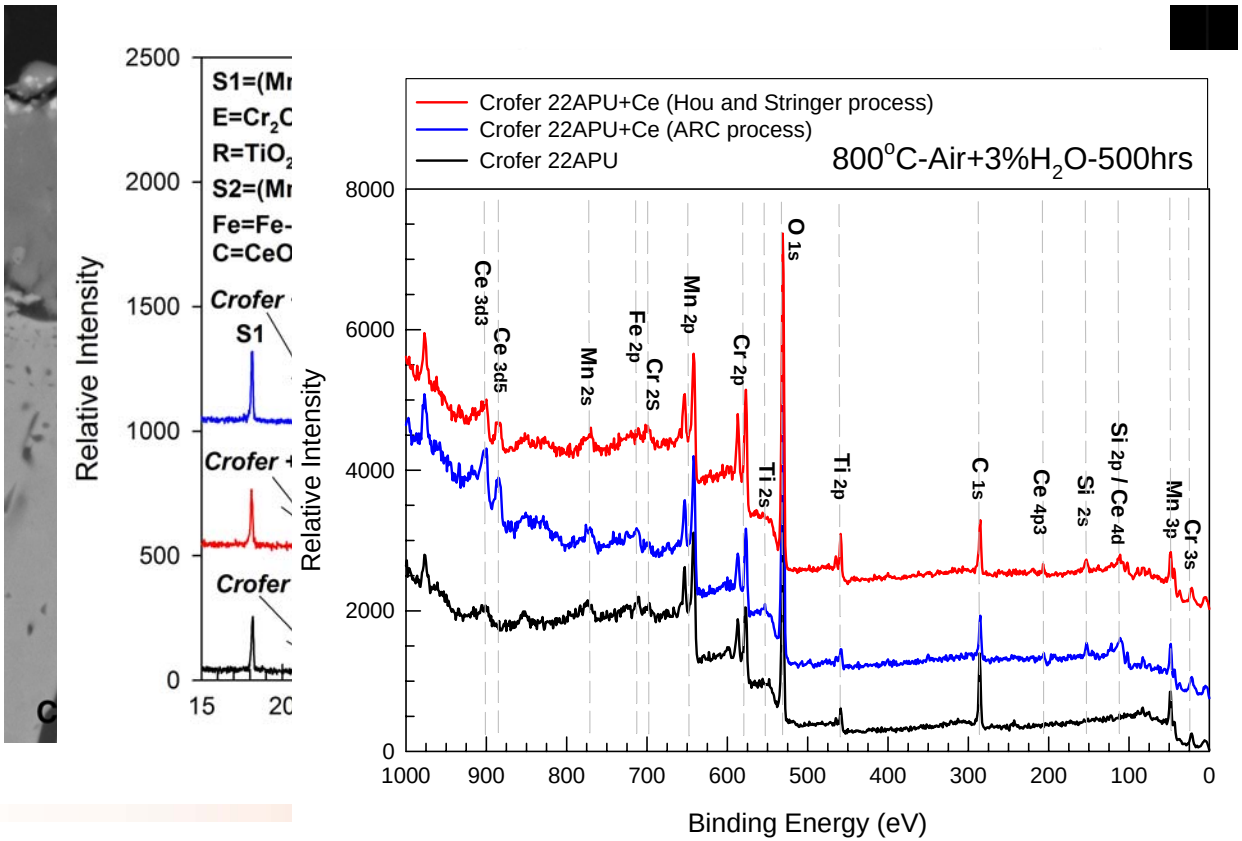
- **Well established that small amounts RE improve oxidation resistance (RE: Ce, La, Y)**
- **Melt addition**
  - + Elements added during ingot production (single manufacturing step)
  - – Difficulty in melting (react with crucibles)
  - – Surface concentration limited by solubility and diffusivity
- **Surface treatments**
  - + Rare Earth concentrated where needed (at surface and have most benefit)
  - – “Extra” manufacturing step.
  - ? Long term effectiveness (as with any coating or surface treatment)

Research Goal

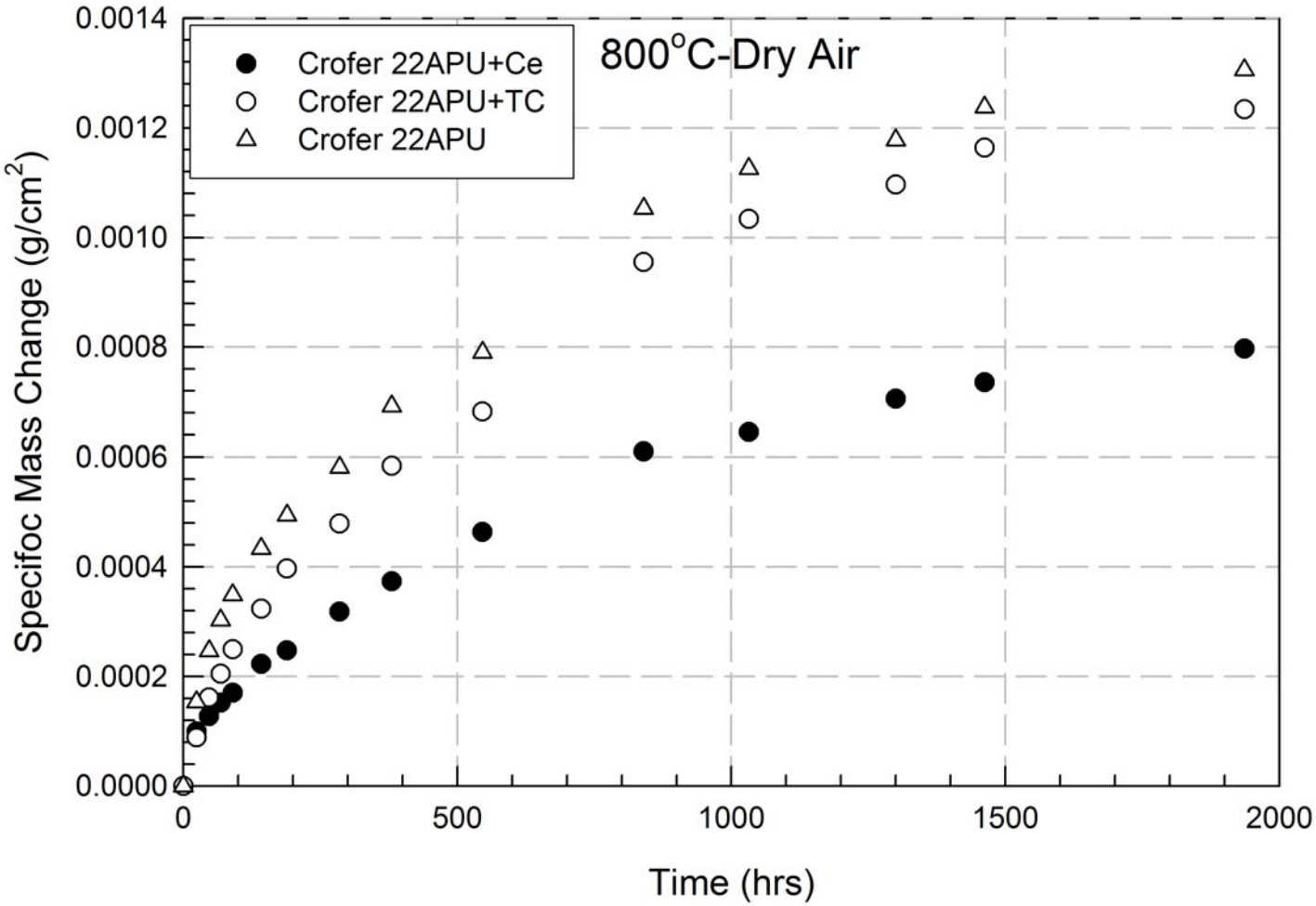
- **Investigate rare earth surface treatment for improving oxidation resistance of alloys for SOFC applications.**
- **Two different surface treatments investigated**
  - Developed at NETL
    - Similar to pack cementation: coated with a powder mixture containing CeO_2 or CeN and halide activator followed by heating in a controlled atmosphere (900^{o}C-12 hrs), after which residual “pack” coating is washed off the surface.
    - Patent application filed with USPTO in September, 2005.
    - Applied to over 50 alloys of interest to FE.
  - Described in a paper by P.Y. Hou and J. Stringer (H/S)
    - J. Electrochem Soc., Vol 134, No. 7, July 1987, pp. 1836-1849
    - Coupons heated to 200^{o}C were coated with a cerium-nitrate slurry (10w/o nitrate adjusted with HNO_3 to pH=2), followed heating in air at 400^{o}C to decompose to CeO_2

Surface Treatments to Improve Oxidation

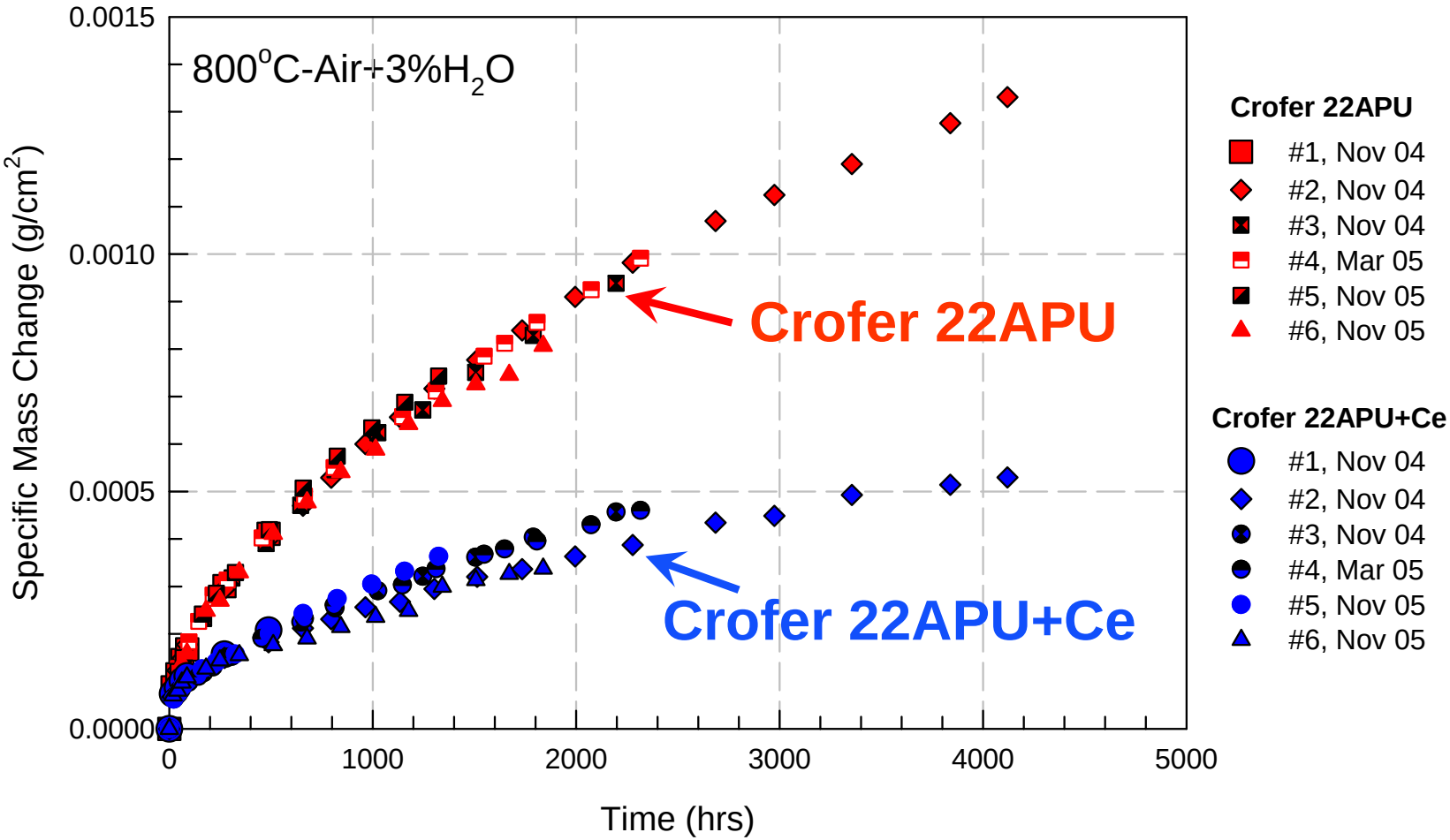
- As part of NETL-Albany's SOFC research effort, we have utilized surface treatments to incorporate reactive elements (Ce, La, Pr) into the surface of metallic alloys for development of metallic interconnects.



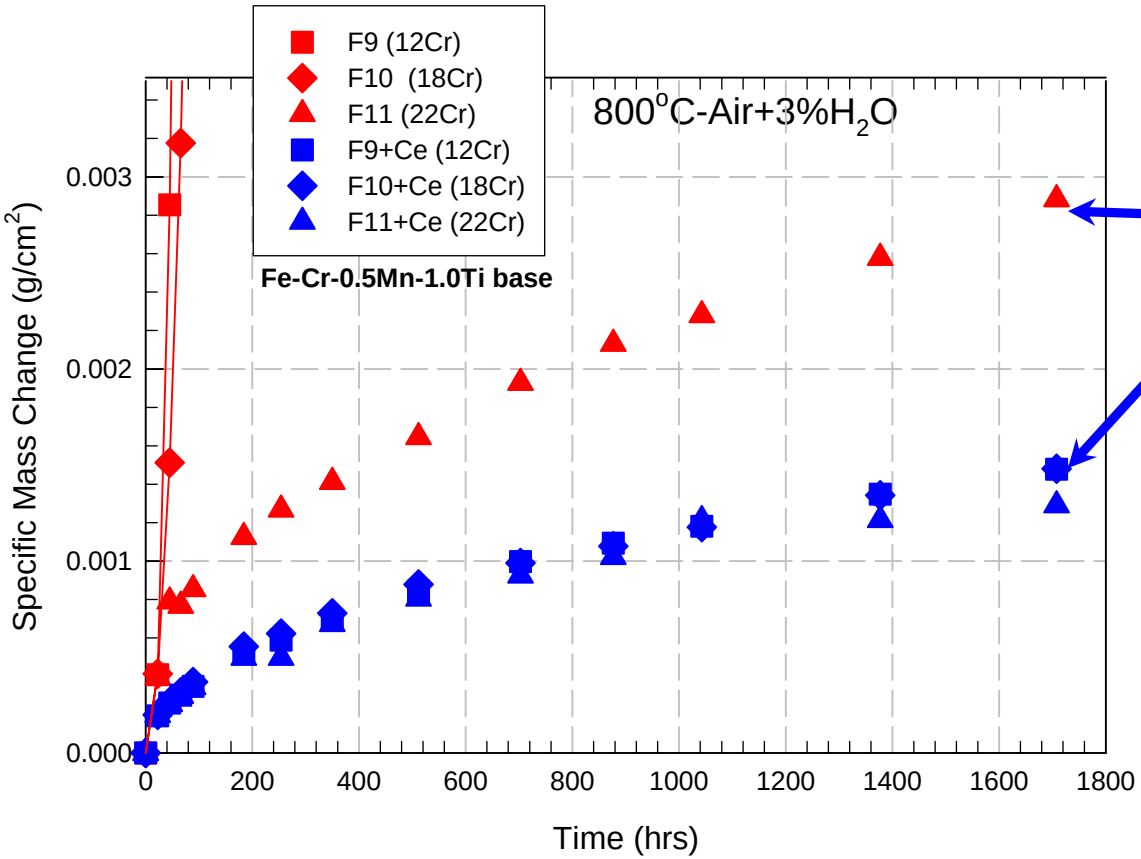
Thermal Treatment (TC) Only is *Ineffective*



Repeatable Behavior

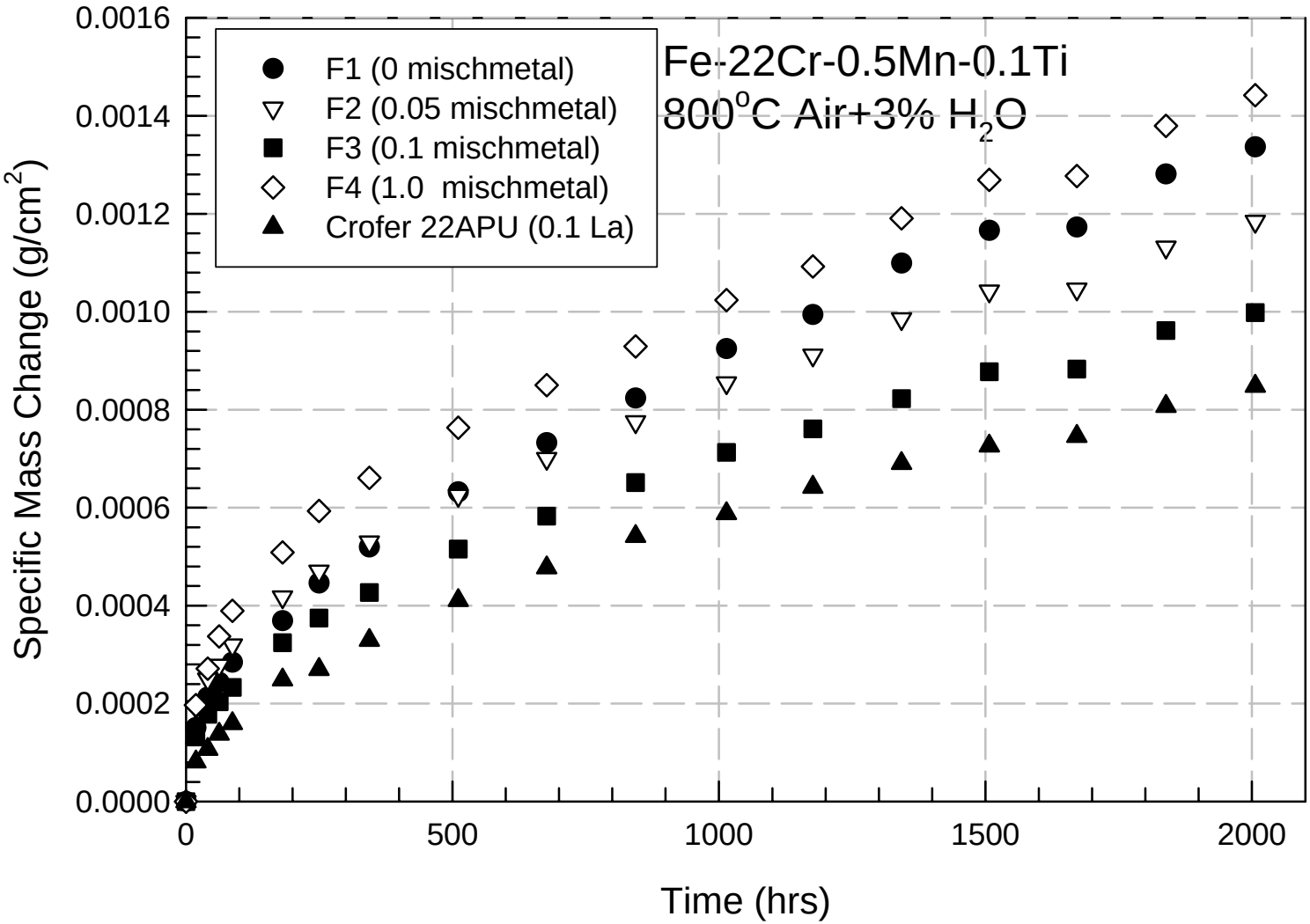


Effect of Ce Treatment: Fe-Ce-0.5Mn-1Ti

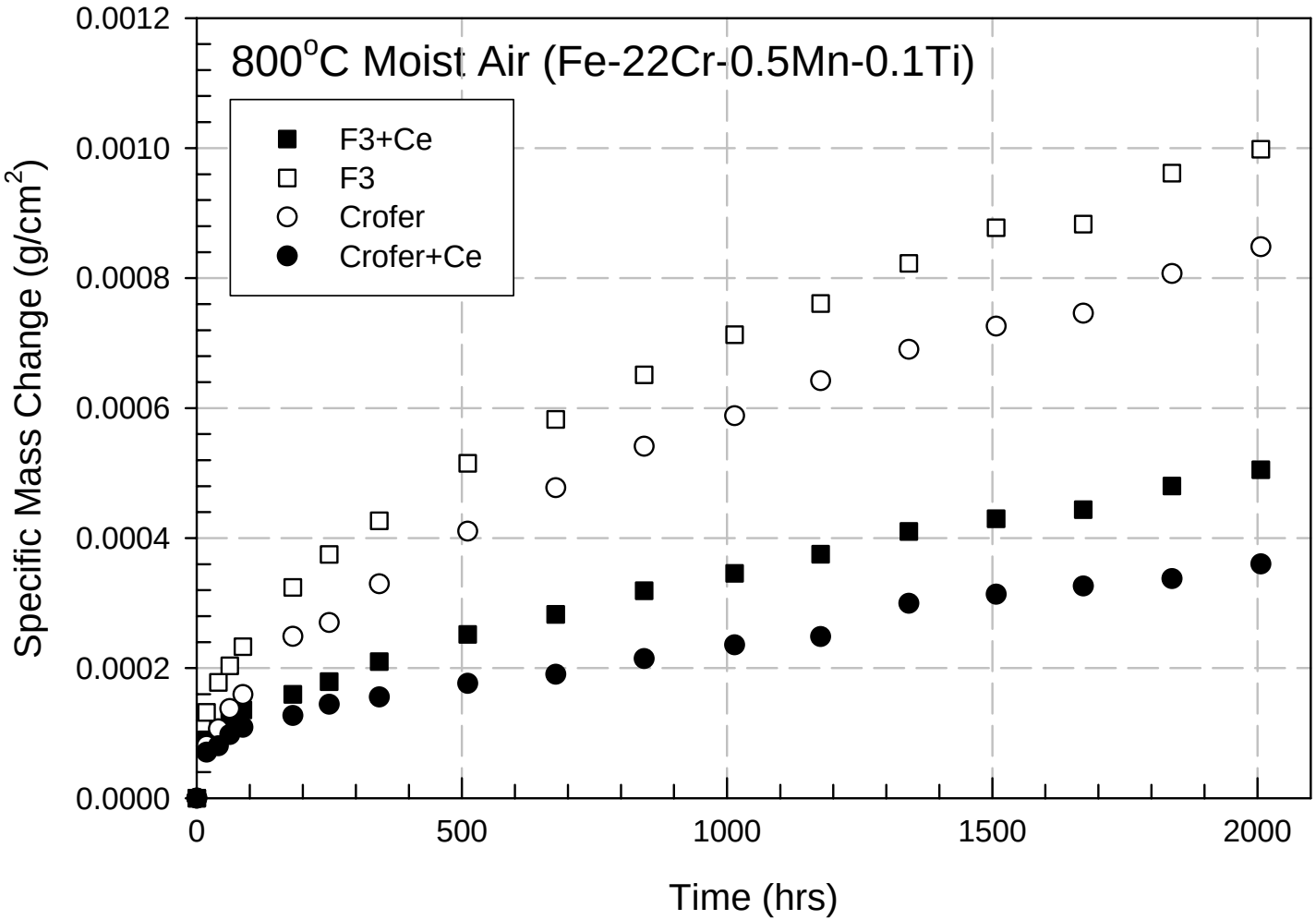


Fe-12Cr + Ce alloy superior performance to an Fe-22Cr alloy

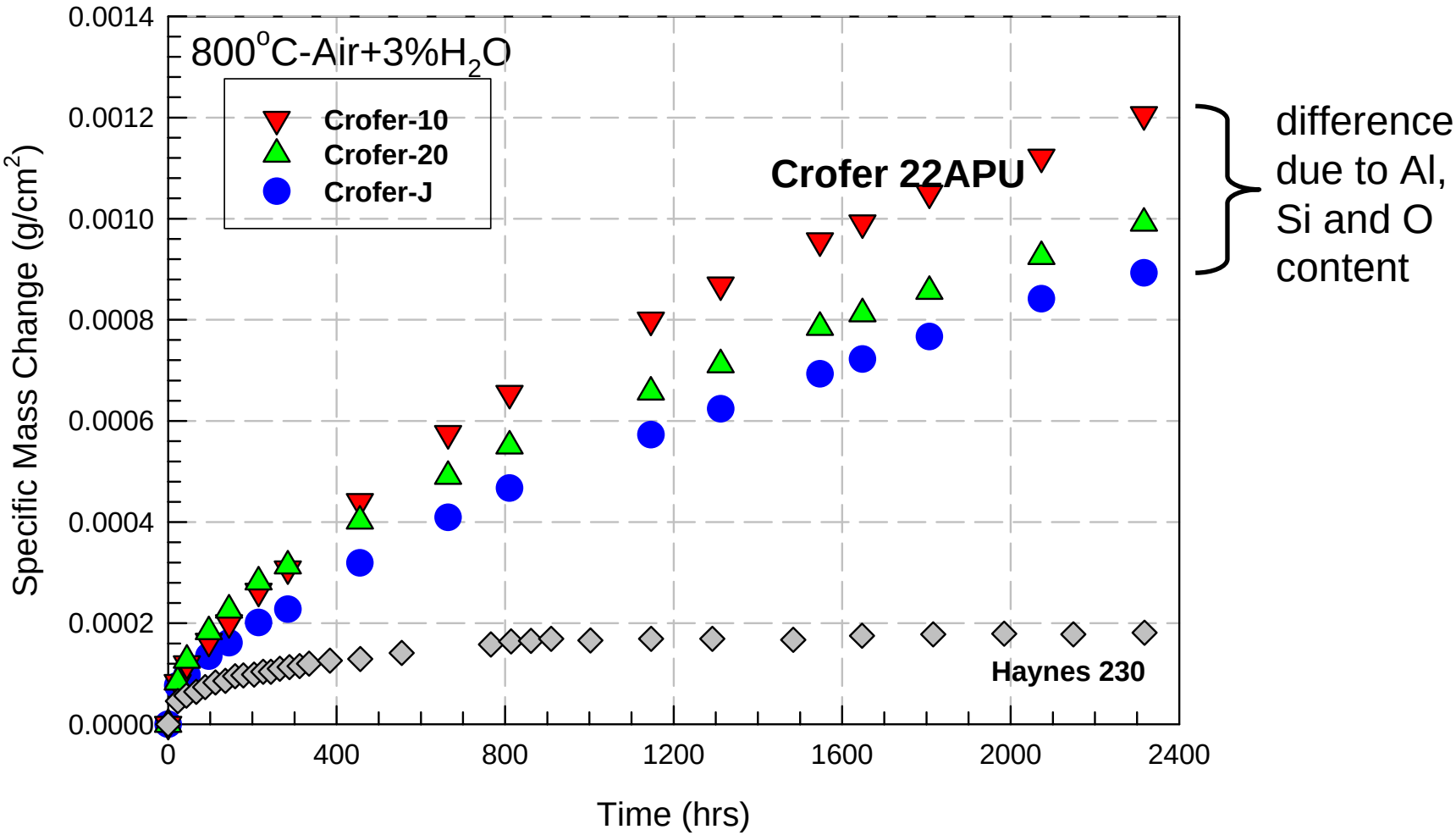
In Melt Additions of RE



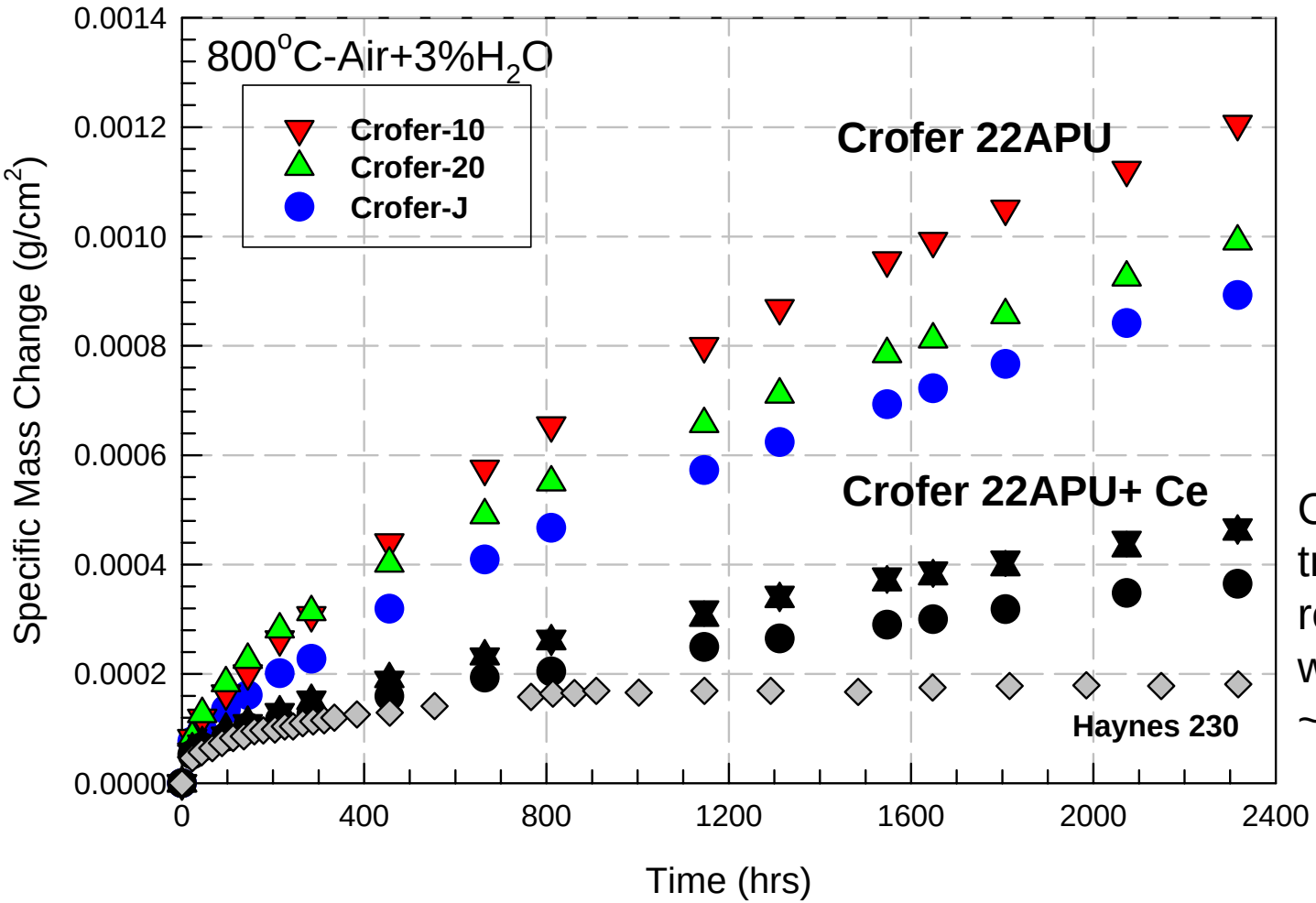
In Melt + Surface Treatment



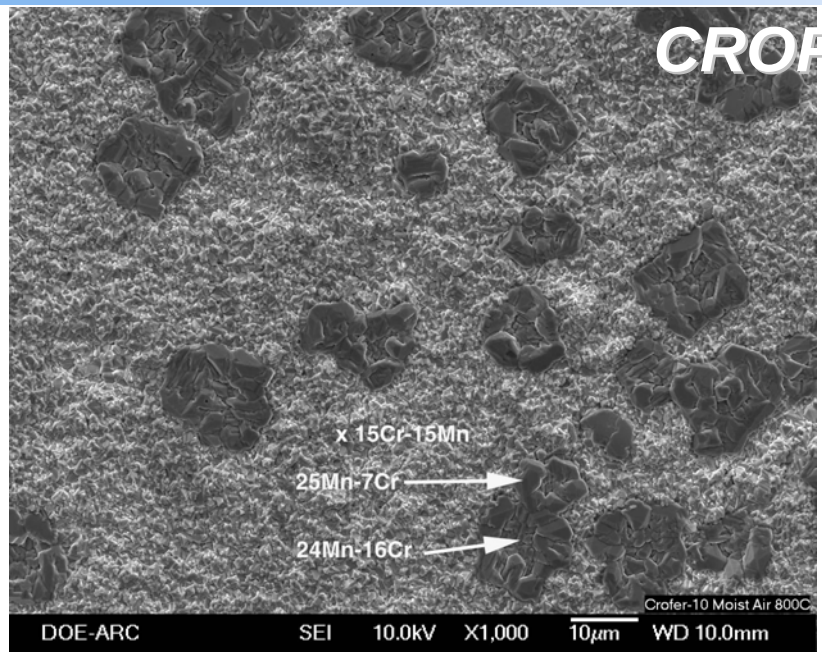
Minor Element Effect

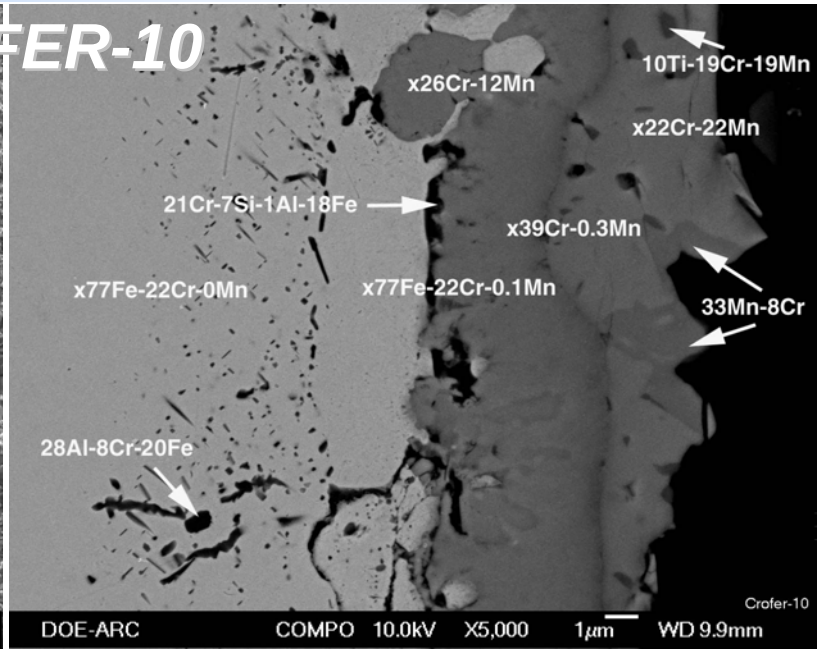


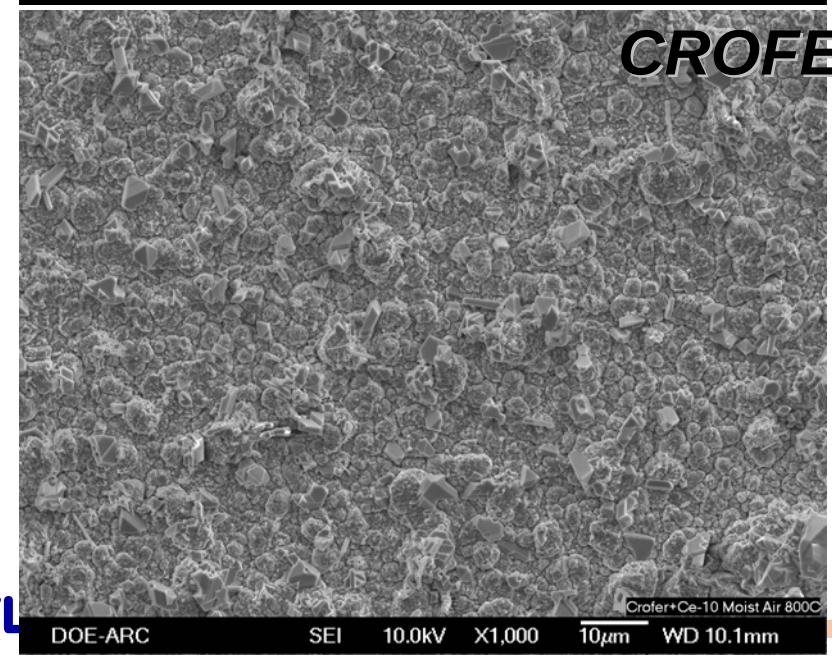
Ce Surface Treatment on Crofer 22APU

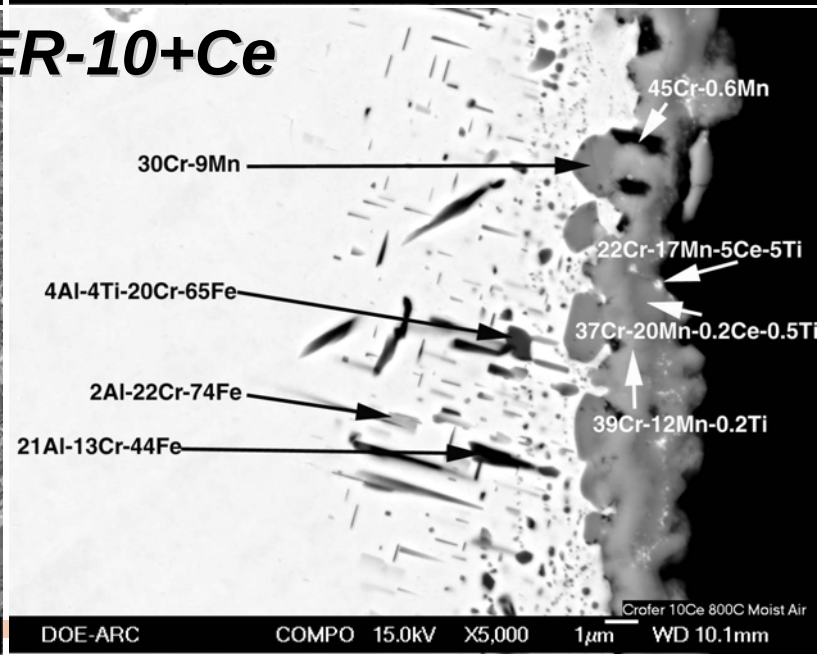


Ce surface treatment reduced weight gain ~ 3 times

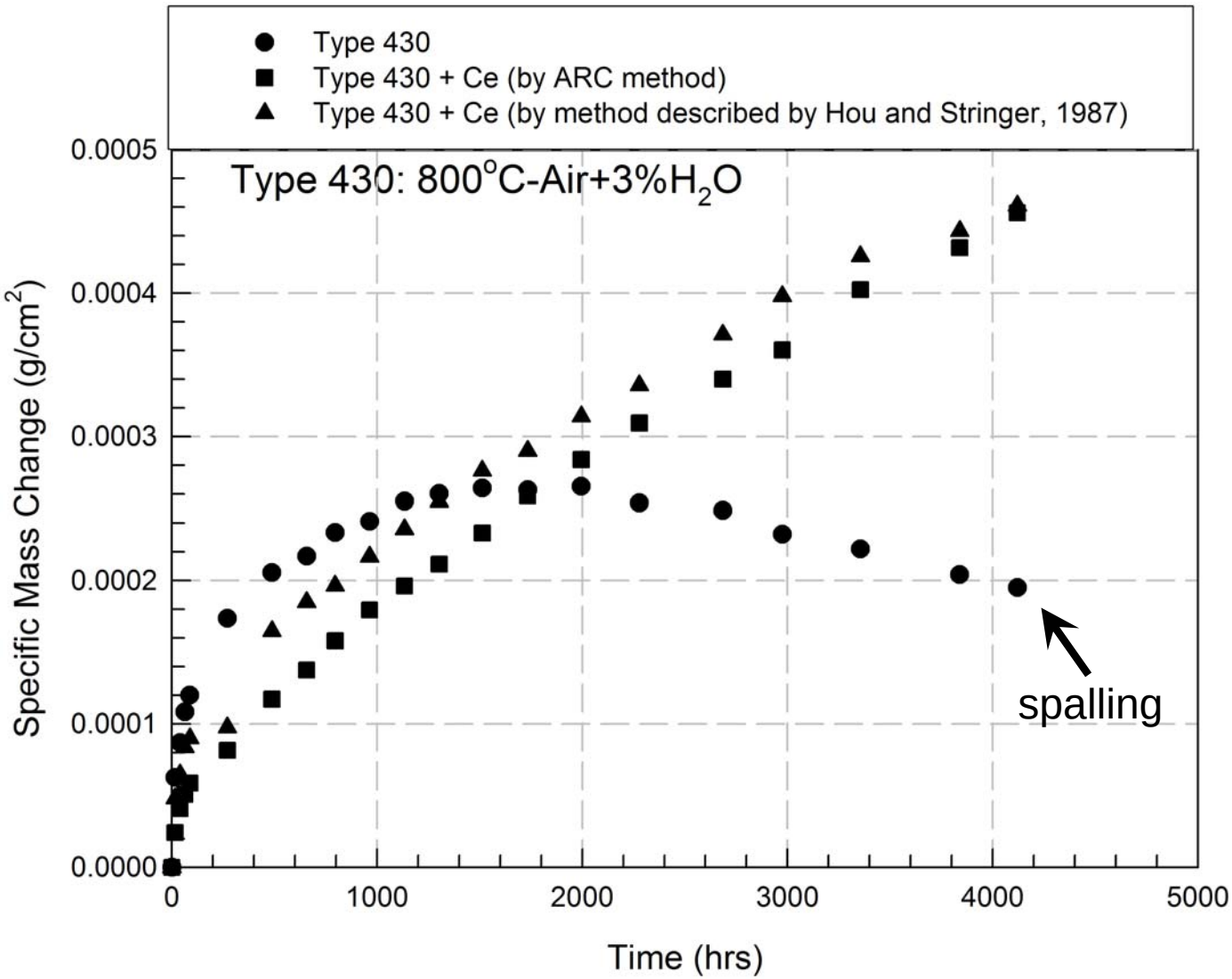

CROFER-10
x 15Cr-15Mn
25Mn-7Cr
24Mn-16Cr
Crofer-10 Moist Air 800C
DOE-ARC SEI 10.0kV X1,000 10μm WD 10.0mm


10Ti-19Cr-19Mn
x26Cr-12Mn
x22Cr-22Mn
21Cr-7Si-1Al-18Fe
x39Cr-0.3Mn
x77Fe-22Cr-0Mn
x77Fe-22Cr-0.1Mn
33Mn-8Cr
28Al-8Cr-20Fe
Crofer-10
DOE-ARC COMPO 10.0kV X5,000 1μm WD 9.9mm


CROFER-10+Ce
Crofer+Ce-10 Moist Air 800C
DOE-ARC SEI 10.0kV X1,000 10μm WD 10.1mm


45Cr-0.6Mn
30Cr-9Mn
22Cr-17Mn-5Ce-5Ti
4Al-4Ti-20Cr-65Fe
37Cr-20Mn-0.2Ce-0.5Ti
2Al-22Cr-74Fe
39Cr-12Mn-0.2Ti
21Al-13Cr-44Fe
Crofer 10Ce 800C Moist Air
DOE-ARC COMPO 15.0kV X5,000 1μm WD 10.1mm

TYPE-430


Type 430
Type 430 + Ce (by ARC method)
Type 430 + Ce (by method described by Hou and Stringer, 1987)
Type 430: 800°C-Air+3%H2O
Specific Mass Change (g/cm2)
0.0000
0.0001
0.0002
0.0003
0.0004
0.0005
0
1000
2000
3000
4000
5000
Time (hrs)
spalling

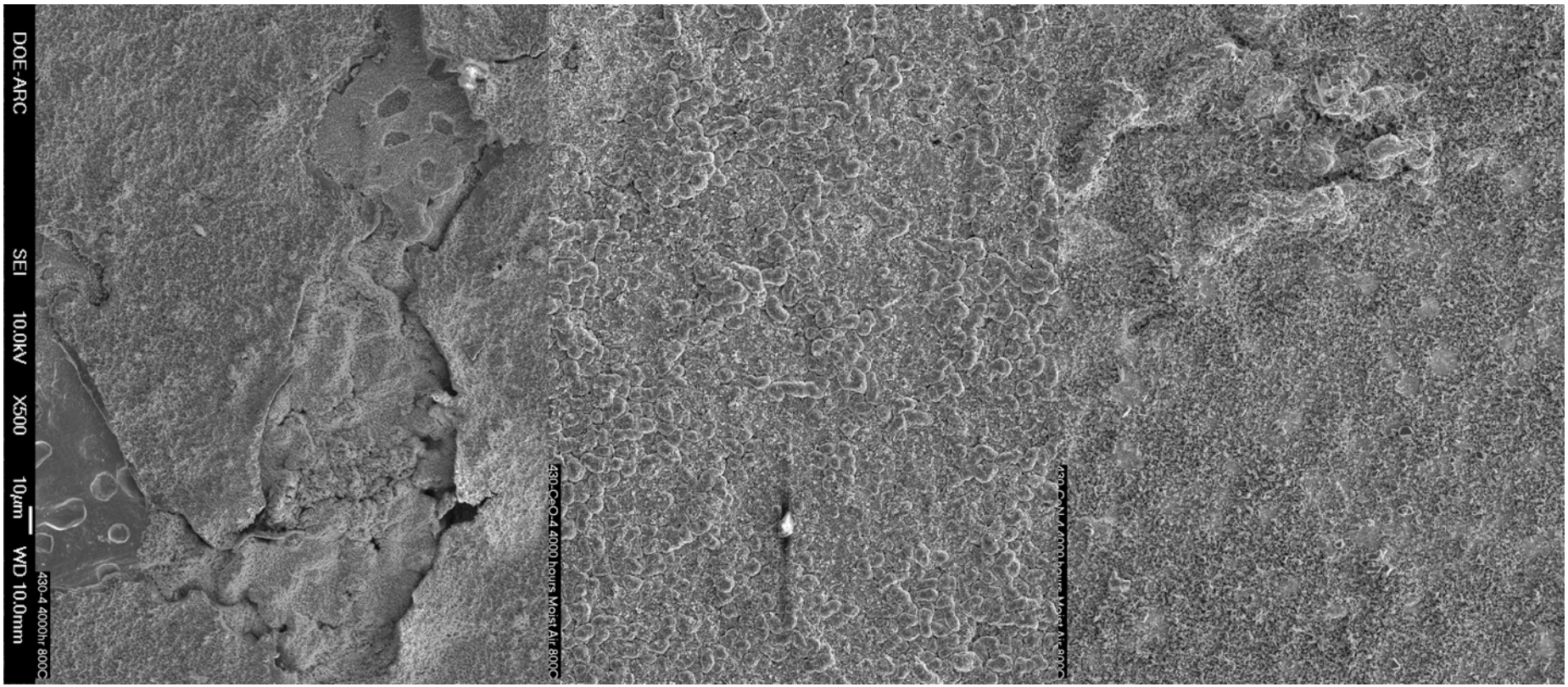
Surface: Type-430

800°C-4000hrs-Air+3%H_2O

430 **430+Ce (ARC)** **430+Ce (H/S)**

Surface: Type-430

800°C-4000hrs-Air+3%H_2O



Type 430

Type 430 + CeO (NETL)

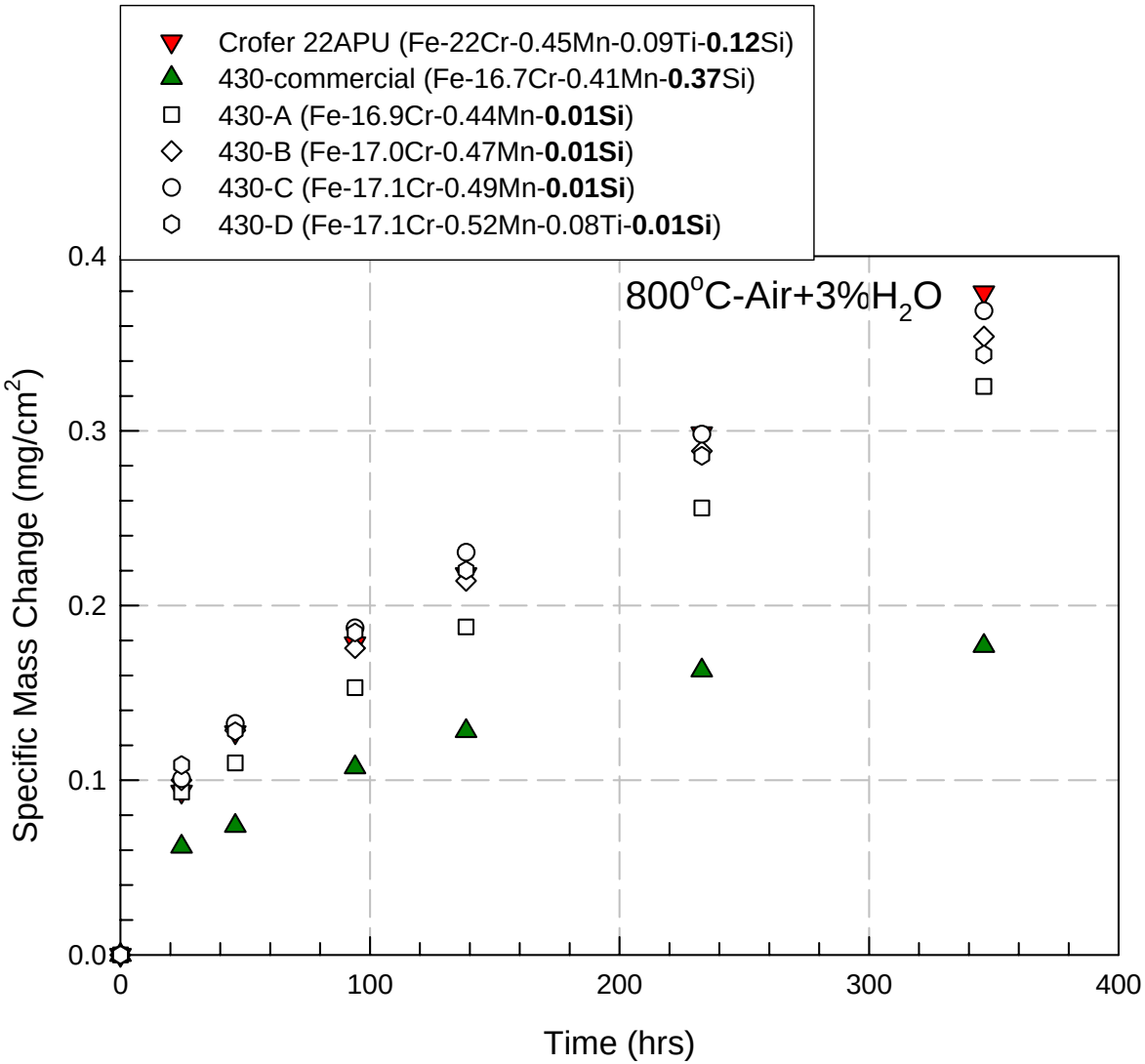
Type 430 + CeO (H/S)

Stainless Steel Alloys

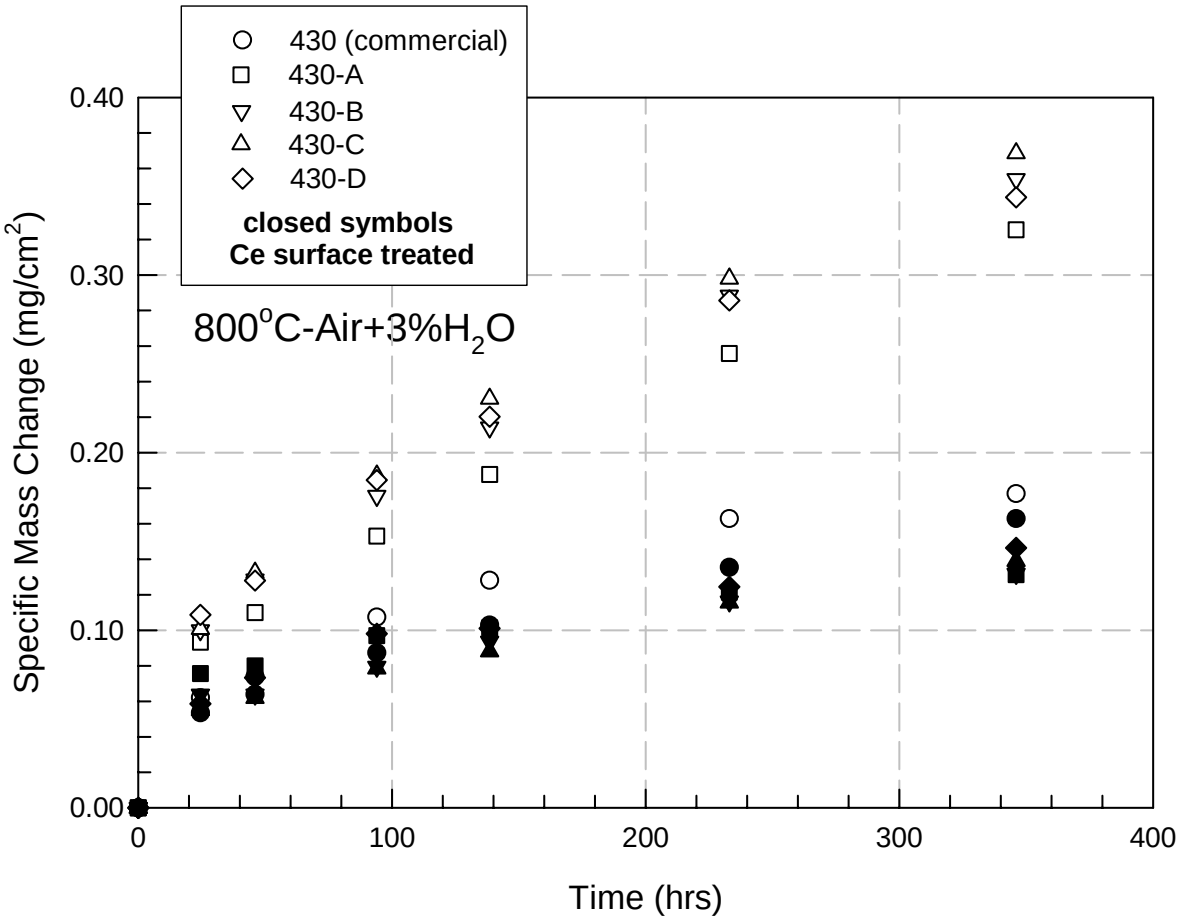
	430-A	430-B	430-C	430-D	430-*std*	Crofer22APU
Fe	Bal	Bal	Bal	Bal	Bal	Bal
Cr	16.85	17.03	17.13	17.11	16.6	22.42
Ti	<0.001	<0.001	<0.001	0.080	<0.001	0.092
Al	<0.001	<0.001	<0.001	<0.001	0.016	0.13
Si	<0.01	<0.01	<0.01	<0.01	0.37	0.12
Mn	0.44	0.47	0.49	0.52	0.42	0.45
C	0.005	0.05	0.1	0.01	0.06	0.02

Alloys 430A-D were melted and fabricated at NETL

Low Si 430 Alloys



Surface Treated Low Si 430 Alloys



Summary

- Oxidation results of a simple surface treatment have been presented.
- The Cerium surface treatment improves the oxidation performance of type 430.
- The Cerium surface treatment improves the oxidation performance of RE containing alloys such as Crofer 22 APU.
- Improved ASR results have been achieved with RE treated Crofer 22 APU.

Acknowledgements

- Gordon Xia and Z. Gary Yang from PNNL for performing the ASR measurements.
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Experimental Alloys and RE Surface Treated Materials Available For Evaluation by SECA Participants